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**WO 03/020836 A1**

(54) Title: FLUOROPOLYMER DISPERSION CONTAINING NO OR LITTLE LOW MOLECULAR WEIGHT FLUORINATED SURFACTANT

(57) Abstract: The present invention provides a fluoropolymer dispersion comprising fluoropolymer particles having an average particle size of 10 to 400nm dispersed in water whereby the dispersion is free of fluorinated surfactant having a molecular weight of less than 1000g/mol or contains the fluorinated surfactant having a molecular weight of less than 1000g/mol in an amount of not more than 0.025% by weight based on the total weight of solids in the dispersion. The dispersion further comprises a non-ionic surfactant and an anionic surfactant selected from fluorinated anionic surfactants having a molecular weight of at least 1000g/mol, non-fluorinated anionic surfactants and mixtures thereof.

**FLUOROPOLYMER DISPERSION CONTAINING NO OR LITTLE LOW MOLECULAR WEIGHT FLUORINATED SURFACTANT****1. Field of the invention.**

5 The present invention relates to aqueous fluoropolymer dispersions that are free of low molecular weight fluorinated surfactant or that contain the latter in low amounts. In particular, the present invention relates to reducing the viscosity of such fluoropolymer dispersions that are high in solids content and that contain non-ionic surfactants as a stabilizer.

**10 2. Background of the invention.**

Fluoropolymers, i.e. polymers having a fluorinated backbone, have been long known and have been used in a variety of applications because of several desirable properties such as heat resistance, chemical resistance, weatherability, UV-stability etc... The various fluoropolymers are for example described in "Modern Fluoropolymers", edited by John Scheirs, Wiley Science 15 1997. The fluoropolymers may have a partially fluorinated backbone, generally at least 40% by weight fluorinated, or a fully fluorinated backbone. Particular examples of fluoropolymers include polytetrafluoroethylene (PTFE), copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) (FEP polymers), perfluoroalkoxy copolymers (PFA), ethylene-tetrafluoroethylene (ETFE) copolymers, terpolymers of tetrafluoroethylene, hexafluoropropylene 20 and vinylidene fluoride (THV) and polyvinylidene fluoride polymers (PVDF).

The fluoropolymers may be used to coat substrates to provide desirable properties thereto such as for example chemical resistance, weatherability, water- and oil repellency etc... For example aqueous dispersions of fluoropolymer may be used to coat kitchen ware, to impregnate fabric or 25 textile e.g. glass fabric, to coat paper or polymeric substrates. For sake of economy and convenience, the fluoropolymer dispersions will typically have between 30% by weight and 70% by weight of fluoropolymer solids.

A frequently used method for producing aqueous dispersions of fluoropolymers involves 30 aqueous emulsion polymerization of one or more fluorinated monomers usually followed by an upconcentration step to increase the solids content of the raw dispersion obtained after the emulsion polymerization. The aqueous emulsion polymerization of fluorinated monomers generally involves the use of a fluorinated surfactant. Frequently used fluorinated surfactants

include perfluoroctanoic acids and salts thereof, in particular ammonium perfluoroctanoic acid. Further fluorinated surfactants used include perfluoropolyether surfactants such as disclosed in EP 1059342, EP 712882, EP 752432, EP 816397, US 6,025,307, US 6,103,843 and US 6,126,849. Still further surfactants that have been used are disclosed in US 5,229,480, US 5,763,552, US 5,688,884, US 5,700,859, US 5,804,650, US 5,895,799, WO 00/22002 and WO 00/71590.

Most of these fluorinated surfactants have a low molecular weight, i.e. a molecular weight of less than 1000g/mol. Recently, such low molecular weight fluorinated compounds have raised environmental concerns. Accordingly, measures have been taken to either completely eliminate the fluorinated low molecular weight surfactants from aqueous dispersion or at least to minimize the amount thereof in an aqueous dispersion. For example, WO 96/24622 and WO 97/17381 disclose an aqueous emulsion polymerization to produce fluoropolymers whereby the polymerization is carried out without the addition of fluorinated surfactant. US 4,369,266 on the other hand discloses a method whereby part of fluorinated surfactant is removed through ultrafiltration. In the latter case, the amount of fluoropolymer solids in the dispersion is increased as well, i.e. the dispersion is upconcentrated while removing fluorinated surfactant. WO 00/35971 further discloses a method in which the amount of fluorinated surfactant is reduced by contacting the fluoropolymer dispersion with an anion exchanger.

20

Since the solids content of the raw dispersions immediately after emulsion polymerization is usually in the range of upto 35% by weight, the raw dispersions are subjected to an upconcentration process so as to increase the solids content thereof. In order to preserve the stability of the dispersion, the upconcentration typically is carried out in the presence of a stabilizer, in particular a non-ionic surfactant that acts as a stabilizer.

25

However, when fluoropolymer dispersions that contain no or only a small amount of fluorinated low molecular weight surfactant are upconcentrated, it was found that a viscosity increase results which may be unacceptable. Moreover, the stability of the upconcentrated dispersions may under certain conditions be inferior to dispersions in which the amount of low molecular weight fluorinated surfactant is higher.

Accordingly, there exists a desire to remove one or more of the aforementioned disadvantages of the prior art.

3. Summary of the invention.

5 According to one aspect of the present invention, there is provided a fluoropolymer dispersion comprising fluoropolymer particles having an average size of 10nm to 400nm dispersed in water whereby the dispersion is free of fluorinated surfactant having a molecular weight of less than 1000g/mol or contains the fluorinated surfactant having a molecular weight of less than 1000g/mol in an amount of not more than 0.025% by weight based on the total weight of solids  
10 in the dispersion. The dispersion further comprises a non-ionic surfactant and an anionic surfactant selected from fluorinated anionic surfactants having a molecular weight of at least 1000g/mol, non-fluorinated anionic surfactants and mixtures thereof.

15 According to a further aspect, the invention also provides a method of providing a fluoropolymer particle dispersion comprising the steps of:

- providing a fluoropolymer dispersion comprising fluoropolymer particles having an average size of 10nm to 400nm comprising fluorinated surfactant having a molecular weight of less than 1000g/mol or being free thereof;
- reducing the amount of the fluorinated surfactant in the dispersion if the amount thereof is more than 0.025% by weight based on the total weight of solids of the dispersion, preferably based on the total weight of fluoropolymer solids in the dispersion;
- upconcentrating the fluoropolymer dispersion in the presence of a non-ionic surfactant so as to increase the amount of fluoropolymer solids in the dispersion; and
- adding an anionic surfactant selected from fluorinated anionic surfactants having a molecular weight of at least 1000g/mol, non-fluorinated anionic surfactants and mixtures thereof, to the fluoropolymer dispersion prior to or after upconcentrating the fluoropolymer dispersion.

20 Still further, the present invention provides a method of coating substrates with the  
25 aforementioned fluoropolymer dispersion of the invention.

4. Detailed description of the invention.

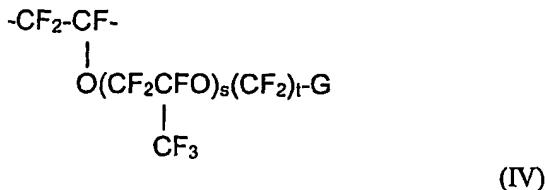
In accordance with the present invention it was found that a viscosity increase of fluoropolymer dispersions that contain a non-ionic surfactant and that are free of low molecular weight fluorinated surfactant or that contain the latter in low amounts, e.g. less than 0.025% by weight (based on the total weight of solids, in particular on the total weight of fluoropolymer solids in the dispersion), preferably not more than 0.01% by weight and most preferably less than 0.005% by weight, can be reduced or avoided if the fluoropolymer dispersion contains an anionic non-fluorinated surfactant, an anionic fluorinated surfactant having a molecular weight of at least 1000g/mol (hereinafter called high molecular weight fluorinated surfactant) or a mixture thereof. Furthermore, the stability of the fluoropolymer dispersion may also be improved by the addition of the anionic non-fluorinated surfactant or anionic high molecular weight fluorinated surfactant.

Preferred anionic non-fluorinated surfactants are surfactants that have an acid group that has a  $pK_a$  of not more than 4, preferably not more than 3. It was found that such anionic surfactants in addition to controlling the viscosity, are generally also capable of increasing the stability of the fluoropolymer dispersion. Examples of non-fluorinated anionic surfactants include surfactants that have one or more anionic groups. Anionic non-fluorinated surfactants may include in addition to one or more anionic groups also other hydrophilic groups such as polyoxyalkylene groups having 2 to 4 carbons in the oxyalkylene group, such as polyoxyethylene groups, or groups such as such as amino groups. Nevertheless, when amino groups are contained in the surfactant, the pH of the dispersion should be such that the amino groups are not in their protonated form. Typical non-fluorinated surfactants include anionic hydrocarbon surfactants. The term "anionic hydrocarbon surfactants" as used herein comprises surfactants that comprise one or more hydrocarbon moieties in the molecule and one or more anionic groups, in particular acid groups such as sulphonic, sulfuric, phosphoric and carboxylic acid groups and salts thereof. Examples of hydrocarbon moieties of the anionic hydrocarbon surfactants include saturated and unsaturated aliphatic groups having for example 6 to 40 carbon atoms, preferably 8 to 20 carbon atoms. Such aliphatic groups may be linear or branched and may contain cyclic structures. The hydrocarbon moiety may also be aromatic or contain aromatic groups. Additionally, the hydrocarbon moiety may contain one or more hetero atoms such as for example oxygen, nitrogen and sulfur.

- Particular examples of anionic hydrocarbon surfactants for use in this invention include alkyl sulfonates such as lauryl sulfonate, alkyl sulfates such as lauryl sulfate, alkylarylsulfonates and alkylarylsulfates, fatty (carboxylic) acids and salts thereof such as lauric acids and salts thereof and phosphoric acid alkyl or alkylaryl esters and salts thereof. Commercially available anionic hydrocarbon surfactants that can be used include Emulsogen™ LS (sodium lauryl sulfate) and Emulsogen™ EPA 1954 (mixture of C<sub>12</sub> to C<sub>14</sub> sodium alkyl sulfates) available from Clariant GmbH and TRITON™ X-200 (sodium alkylsulfonate) available from Union Carbide. Preferred are anionic hydrocarbon surfactants having a sulfonate group.
- Other suitable anionic non-fluorinated surfactants include silicone based surfactants such as polydialkylsiloxanes having pending anionic groups such as phosphoric acid, groups, carboxylic acid groups, sulfonic acid groups and sulfuric acid groups and salts thereof.
- Alternative to or in addition to the anionic non-fluorinated surfactant, a high molecular weight fluorinated surfactant can be used. The high molecular weight fluorinated surfactant has a molecular weight of at least 1000g/mol, preferably at least 1200g/mol. Examples of high molecular weight anionic and fluorinated surfactants comprise polymeric surfactants and include perfluoropolyethers having one or more anionic groups such as carboxylic acid groups or salts thereof. Examples of perfluoropolyether surfactants include those according to the following formulas (I) or (II):
- $$R_f^a-O-(CF_2O)_k(CF_2CF_2O)_p(CF(CF_3)CF_2O)_q-Q^1-COOM \quad (I)$$
- $$MOOC-Q^1-O-(CF_2O)_k(CF_2CF_2O)_p(CF(CF_3)CF_2O)_q-Q^2-COOZ \quad (II)$$
- wherein k, p and q each represent a value of 0 to 15, typically 0 to 10 or 12 and the sum of k, p and q being such that the number average molecular weight is at least 1000g/mol, R<sub>f</sub><sup>a</sup> represents a perfluoroalkyl group preferably of 2 to 4 carbon atoms, M and Z each independently represent hydrogen or a cation, preferably a monovalent cation such as ammonium or an alkali metal ion and Q<sup>1</sup> and Q<sup>2</sup> each independently represents -CF<sub>2</sub>- or -CF(CF<sub>3</sub>)-.
- Examples of fluorinated surfactants of formula (II) include those corresponding to the formula:
- $$R_f^a-O-(CFXCF_2O)_r-CFX-COOM \quad (III)$$

wherein  $R_f^a$  and M have the meaning as defined in formula (II), X is a hydrogen atom or a fluorine atom and r has a value such that the molecular weight of the surfactant is at least 1000g/mol. Examples of such fluorinated surfactants are disclosed in EP 219065.

- 5 Still further fluorinated polymeric surfactants that can be used include the perfluoropolymers that comprise repeating units of the formula:



wherein s is 0, 1 or 2, and t is an integer of 2 to 4, and G is a moiety containing one or more anionic groups. Examples of suitable anionic groups include: carboxyl groups, e.g.,  $-\text{CO}_2\text{M}$

10 where M may be hydrogen, a mono or divalent metal ion (e.g., sodium, potassium or magnesium), ammonium (e.g., simple ammonium, tetraalkylammonium, tetraarylammonium) or phosphonium (e.g., tetraalkylphosphonium); or sulfonate groups, e.g.,  $-\text{SO}_3\text{M}$ , where M is defined as above. Preferably, the fluorinated polymeric surfactant is a copolymer having units derived from tetrafluoroethylene and units according to formula (IV). Such copolymers and their method of making are disclosed in for example US 5,608,022 and WO 00/52060. Suitable fluorinated polymeric surfactants are available as Nafion™ superacid catalysts from E. I duPont de Nemours & Co., Wilmington, DE and are also available as Flemion™ superacid polymers from Asahi Chemical Co., Osaka, Japan and as Acipex™ superacid polymers from Asahi Glass Co., Tokyo, Japan.

20 The amount of anionic surfactant added to the fluoropolymer dispersion will generally depend on the nature of the fluorinated surfactant, nature and amount of the fluoropolymer, nature and amount of non-ionic surfactant present in the dispersion and nature and amount of low molecular weight fluorinated surfactant that may be present in the fluoropolymer dispersion. Typically, the amount of anionic surfactant will be between 10ppm and 5000ppm, preferably between 100ppm and 3000ppm, more preferably between 100ppm and 2500ppm based on the weight of the fluoropolymer solids in the dispersion. When too low amounts of the anionic surfactant are used, an undesirable viscosity increase may still be observed. On the other hand, when too large

amounts of the anionic surfactant are added the viscosity may also raise. If it is further desired or needed to increase the stability of the dispersion, it may be necessary to use the anionic surfactant in an amount of at least 2000ppm based on the weight of fluoropolymer solids. The optimal concentration of the anionic surfactant in the dispersion can be easily determined by one skilled in the art through routine experimentation.

The low molecular weight fluorinated surfactant, when present, may be any of the low molecular weight fluorinated surfactants that can be used in the emulsion polymerization of fluorinated monomers and include in particular those that have been mentioned above in respect of the discussion of the prior art. Commonly used low molecular weight fluorinated surfactants are telogenic and include those that correspond to the formula:

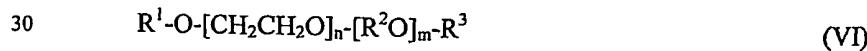


wherein Y represents hydrogen, Cl or F; R<sub>f</sub> represents a linear or branched perfluorinated alkylene having 4 to 10 carbon atoms; Z represents COO<sup>-</sup> or SO<sub>3</sub><sup>-</sup> and M represents a monovalent cation such as an alkali metal ion or an ammonium ion.

The low molecular weight fluorinated surfactant, when present in the fluoropolymer dispersion, may be present in amounts of less than 0.025% by weight, preferably not more than 0.01% by weight and most preferably not more than 50ppm based on the total amount of solids in the dispersion.

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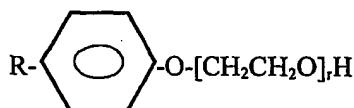
The fluoropolymer dispersion of the present invention also includes a non-ionic surfactant. The non-ionic surfactant is generally a non-fluorinated non-ionic surfactant. Typically, the non-ionic surfactant is a surfactant that contains one or more hydrocarbon moieties, e.g. as described above, linked to a non-ionic hydrophilic group. The non-ionic hydrophilic group generally comprises oxyalkylene groups in which the alkylene group has 2, 3 or 4 carbon atoms. For example, the non-ionic hydrophilic group may be a polyoxyethylene group, a polyoxypropylene group or a copolymer, including block-copolymers, comprising oxyethylene and oxypropylene groups. According to a particular embodiment in connection with the present invention, the non-ionic surfactant corresponds to the formula:



wherein R<sup>1</sup> represents an aromatic or aliphatic hydrocarbon group having at least 8 carbon atoms, R<sup>2</sup> represents an alkylene having 3 carbon atoms, R<sup>3</sup> represents hydrogen or a C<sub>1</sub>-C<sub>3</sub> alkyl group, n has a value of 0 to 40, m has a value of 0 to 40 and the sum of n+m being at least 2.

- 5 It will be understood that in the above formula (VI), the units indexed by n and m may appear as blocks or they may be present in an alternating or random configuration.

Examples of non-ionic surfactants according to formula (VI) above include alkylphenol oxy ethylates of the formula:



10

(VII)

wherein R is an alkyl group of 4 to 20 carbon atoms and r represents a value of 4 to 20.

Examples of surfactants according to formula (VII) include ethoxylated p-isoctylphenol commercially available under the brand name TRITON™ such as for example TRITON™ X 100 wherein the number of ethoxy units is about 10 or TRITON™ X 114 wherein the number of ethoxy units is about 7 to 8.

15

Still further examples include those in which R<sup>1</sup> in the above formula (VI) represents an alkyl group of 4 to 20 carbon atoms, m is 0 and R<sup>3</sup> is hydrogen. An example thereof includes isotridecanol ethoxylated with about 8 ethoxy groups and which is commercially available as GENAPOL® X 080 from Clariant GmbH. Non-ionic surfactants according to formula (VI) in which the hydrophilic part comprises a block-copolymer of ethoxy groups and propoxy groups may be used as well. Such non-ionic surfactants are commercially available from Clariant GmbH under the trade designation GENAPOL® PF 40 and GENAPOL® PF 80.

20

25 The non-ionic surfactant is generally present in the fluoropolymer dispersion in an amount of 1% by weight to 12% by weight relative to the total weight of solids in the fluoropolymer dispersion. Preferably the amount is between 3% by weight and 10% by weight.

The fluoropolymer contained in the fluoropolymer dispersion is a polymer that has a partially or fully fluorinated backbone. Typically the fluoropolymer is a polymer that has a backbone that is at least 40% by weight fluorinated, preferably at least 50% by weight, more preferably at least 5 60% by weight. The fluoropolymer may also have a fully fluorinated backbone such as for example in PTFE. The fluoropolymer may be a homo- or copolymer and the dispersion may contain a mixture of different fluoropolymers. Examples of fluoropolymers include copolymers of tetrafluoroethylene which can be processed from the melt, especially those of tetrafluoroethylene/hexafluoropropylene, tetrafluoroethylene/perfluoro(alkylvinyl) ethers with perfluoroalkyl radicals having 1 to 5 C atoms, in particular perfluoro(n-propyl-vinyl) ethers, tetrafluoroethylene/ethylene, tetrafluoroethylene/trifluorochloroethylene, trifluorochloroethylene/ethylene, tetrafluoroethylene/vinylidene fluoride and hexafluoropropylene/vinylidene fluoride, and terpolymers of tetrafluoroethylene/perfluoro(alkylvinyl) ether/hexafluoropropylene, 10 tetrafluoroethylene/ethylene/hexafluoropropylene and tetrafluoroethylene/vinylidene fluoride/hexafluoropropylene, or of quaternary polymers of tetrafluoroethylene/vinylidene fluoride/hexafluoropropylene/perfluoro(alkylvinyl) ethers and tetrafluoroethylene/ethylene/hexafluoropropylene/ perfluoro(alkylvinyl) ethers. Further 15 fluoropolymers that can be used in the dispersion include polyvinyl fluoride, polyvinylidene fluoride and polytrifluorochloroethylene. The dispersion may also comprise polymers that cannot be processed from the melt such as polytetrafluoroethylene, that is to say of the homopolymer and which can optionally contain modifying comonomers, such as hexafluoropropylene or perfluoro(alkylvinyl) ethers or chlorotrifluoroethylene, in small proportions (0.1 to 3 mol %). 20

25 The average particle size (average particle diameter) of the fluoropolymer in the dispersion is generally in the range of 10nm to 400nm, preferably between 25nm and 400nm. The average particle diameter is generally determined through dynamic light scattering and a number average particle diameter may thereby be determined. The dispersion may be mono-modal as well as multi-modal such as bimodal. The amount of fluoropolymer in the dispersion is typically at least 30 30% by weight, for example between 35% by weight and 70% by weight.

The fluoropolymer dispersions can be used to coat a substrate. For example the fluoropolymer dispersions may be used to coat a metal substrate, polymeric substrates such as polyester and polypropylene substrates or to coat paper. The fluoropolymer dispersions may also be used to coat or impregnate textile or fabrics, in particular glass fiber substrates. Before coating, the 5 fluoropolymer dispersion may be mixed with further ingredients to prepare a coating composition as may be desired for the particular coating application. For example, the fluoropolymer dispersion may be combined with polyamide imide and polyphenylene sulfone resins as disclosed in for example WO 94/14904 to provide anti-stick coatings on a substrate. Further coating ingredients include inorganic fillers such as colloidal silica, aluminium oxide, 10 and inorganic pigments as disclosed in for example EP 22257 and US 3,489,595.

The fluoropolymer dispersions are generally obtained by starting from a so-called raw dispersion, which may result from an emulsion polymerization of fluorinated monomer. Such dispersion may be free of low molecular weight fluorinated surfactant if the polymerization has 15 been conducted in the absence of a low molecular weight fluorinated surfactant but will generally contain substantial amounts of low molecular weight fluorinated surfactant. If the concentration of low molecular weight fluorinated surfactant in the dispersion is more than a desired level, e.g. above 0.025% by weight, at least part thereof should be removed.

According to one embodiment to reduce the amount of low molecular weight of fluorinated 20 surfactant, a non-ionic surfactant, e.g. as disclosed above is added to the fluoropolymer dispersion and the fluoropolymer dispersion is then contacted with an anion exchanger. Such a method is disclosed in detail in WO 00/35971. Suitable anion exchangers include those that have a counterion corresponding to an acid having a pK<sub>a</sub> value of at least 3.

25 The anion exchange process is preferably carried out in essentially basic conditions. Accordingly, the ion exchange resin will preferably be in the OH<sup>-</sup> form although anions like fluoride or oxalate corresponding to weak acids may be used as well. The specific basicity of the ion exchange resin is not very critical. Strongly basic resins are preferred because of their higher 30 efficiency in removing the low molecular weight fluorinated surfactant. The process may be carried out by feeding the fluoropolymer dispersion through a column that contains the ion exchange resin or alternatively, the fluoropolymer dispersion may be stirred with the ion

exchange resin and the fluoropolymer dispersion may thereafter be isolated by filtration. With this method, the amount of low molecular weight fluorinated surfactant can be reduced to levels below 150ppm or even below 10ppm. Accordingly, dispersions substantially free of low molecular weight fluorinated surfactant may thereby be obtained.

5

In case the low molecular weight fluorinated surfactant is in its free acid form is steam-volatile, the following method may be used to reduce the amount of low molecular weight fluorinated surfactant. A steam-volatile fluorinated surfactant in its free acid form may be removed from aqueous fluoropolymer dispersions, by adding a nonionic surfactant to the aqueous fluoropolymer dispersion and, at a pH-value of the aqueous fluoropolymer dispersion below 5, removing the steam-volatile fluorinated surfactant by distillation until the concentration of steam-volatile fluorinated surfactant in the dispersion reaches the desired value. Low molecular weight fluorinated surfactant that can be removed with this process include for example the surfactants according to formula (V) above.

10

It will generally be desirable to increase the amount of fluoropolymer solids in the dispersion. To increase the amount of fluoropolymer solids, any of the upconcentration techniques may be used. These upconcentration techniques are typically carried out in the presence of a non-ionic surfactant which is added to stabilize the dispersion in the upconcentration process. The amount 20 of non-ionic surfactant that should generally be present in the dispersion for upconcentration is typically between 1% by weight and 12% by weight, preferably between 3% by weight and 10% by weight. Suitable methods for upconcentration include ultrafiltration, thermal upconcentration, thermal decantation and electrodecantation as disclosed in GB 642,025.

25

The method of ultrafiltration comprises the steps of (a) adding non-ionic surfactant to a dispersion that desirably is to be upconcentrated and (b) circulating the dispersion over a semi-permeable ultra-filtration membrane to separate the dispersion into a fluorinated polymer dispersion concentrate and an aqueous permeate. The circulation is typically at a conveying rate of 2 to 7 meters per second and effected by pumps which keep the fluorinated polymer free from 30 contact with components which cause frictional forces. The method of ultrafiltration further has the advantage that during upconcentration also some low molecular weight fluorinated surfactant

is removed. Accordingly, the method of ultrafiltration may be used to simultaneously reduce the level of low molecular weight fluorinated surfactant and upconcentrate the dispersion.

To increase the fluoropolymer solids in the aqueous dispersion, thermal decantation may also be employed. In this method, a non-ionic surfactant is added to the fluoropolymer dispersion that is desirably upconcentrated and the dispersion is then heated so as to form a supernatant layer that can be decanted and that typically contains water and some non-ionic surfactant while the other layer will contain the concentrated dispersion. This method is for example disclosed in US 3,037,953 and EP 818506.

10

Thermal upconcentration involves heating of the dispersion and removal of water under a reduced pressure until the desired concentration is obtained.

In accordance with the present invention, the anionic surfactant to control viscosity is added prior to or after the upconcentration depending on the method of upconcentration used. For example, if ultrafiltration is used, it will generally be preferred to add the anionic surfactant subsequent to the upconcentration to avoid loss thereof in the ultrafiltration. If the thermal upconcentration method is used, the anionic surfactant can be added prior to the upconcentration as well as subsequent to the upconcentration.

20

## EXAMPLES

Abbreviations:

PTFE= polytetrafluoroethylene

APFOA= ammonium salt of perfluorooctanoic acid

25 TRITON<sup>TM</sup> X-100= ethoxylated p-isoctylphenol non-ionic surfactant

EMULSOGEN<sup>TM</sup> LS= sodium lauryl sulfate

TRITON<sup>TM</sup> X-200= sodium alkylarylpolyether sulfonate

Test methods:

30 The viscosity of the dispersions was measured using a Brookfield Rheometer DV-III, spindle 86 at 20°C and 20 D/l/s.

**Stability test:**

The fluoropolymer dispersion was mixed and agitated with additional components to formulate a coating composition as disclosed in EP 894541. To this end, the fluoropolymer dispersion was mixed with an aqueous composition containing a polyamideimide resin (PAI) such that the  
5 weight ratio of fluoropolymer solids to PAI solids was 1:1.

Mixing was carried out with a blade agitator at 800 rpm. The time until coagulation occurred was noted.

**Comparative Example 1:**

10 A fluoropolymer dispersion of PTFE of a particle size of about 220nm and having a solids content between 23% by weight was obtained from an emulsion polymerization. To the dispersion were added 6% by weight of TRITON™ X-100. The dispersion contained about 0.1% by weight of APFOA based on total weight of the dispersion (=4350ppm based on polymer solids). The dispersion was upconcentrated through ultrafiltration to an amount of PTFE solids  
15 of 60% by weight. The resulting dispersion had a viscosity of 20mPa.

**Comparative Example 2:**

The procedure of comparative example 1 was repeated except that the dispersion obtained after the emulsion polymerization was contacted with an anion exchange resin so as to reduce the  
20 amount of APFOA in the dispersion to 7ppm based on total weight of the dispersion (=30ppm based on polymer solids). This dispersion was then upconcentrated as described in comparative example 1. It was found that the viscosity of the dispersion was increased to 101mPa. The dispersion had a too high viscosity for coating substrates such as metal substrates or glass cloth because of bubble building.

25

**Example 1:**

To the dispersion obtained in comparative example 2 after upconcentration, there was added 2000ppm based on the solids amount of EMULSOGEN™ LS. The viscosity of the dispersion thereby decreased to 16.7mPa. The dispersion thus obtained is suitable for coating for example  
30 metal substrates.

**Example 2:**

To the dispersion obtained in comparative example 2 after upconcentration, there was added 1500ppm based on the solids amount of TRITON™ X-200. The viscosity of the dispersion thereby decreased to 18mPa. The dispersion thus obtained is suitable for coating for example metal substrates.

5

**Comparative Example 3:**

A PTFE dispersion having 7 ppm APFOA was upconcentrated to 58% solids in the presence of 5% of TRITON™ X-100. The obtained dispersion was tested for stability. Immediately 10 coagulation occurred.

10

**Example 3:**

A dispersion was produced as in example 1 but with the difference that only 1500ppm of EMULSOGEN™ LS was used. Coagulation occurred after about 1 hour.

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**Example 4:**

A dispersion was produced as in example 1 but with the difference that only 3000ppm of EMULSOGEN™ LS was used. No coagulation occurred during at least 20 hours of agitation.

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**Comparative Example 4:**

A dispersion of PTFE containing 7 ppm of APFOA (based on total weight of the dispersion) and 8.5% by weight based on total weight of solids, of non-ionic surfactant was prepared. The dispersion had a solids amount of 59% by weight based on the total weight of the dispersion. The viscosity of this dispersion was 275 mPas and as a result, coating of glass cloth was not 25 possible because of air entrapment.

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**Example 5:**

A PTFE dispersion as in comparative example 4 was prepared and 3000ppm (based on total solids) of EMULSOGEN™ LS were added. The viscosity of this dispersion was only 37 mPas 30 allowing the coating of glass cloth without air entrapment.

**CLAIMS**

1. Fluoropolymer dispersion comprising fluoropolymer particles having an average particle size of 10 to 400nm dispersed in water, said dispersion being free of fluorinated surfactant having a molecular weight of less than 1000g/mol or containing said 5 fluorinated surfactant having a molecular weight of less than 1000g/mol in an amount of not more than 0.025% by weight based on the total weight solids of said dispersion, said dispersion further comprising a non-ionic surfactant characterized in that said dispersion contains an anionic surfactant selected from fluorinated anionic surfactants having a molecular weight of at least 1000g/mol, non-fluorinated anionic surfactants and mixtures 10 thereof.
2. Fluoropolymer dispersion according to claim 1 wherein the anionic surfactant is present in an amount of 100 to 5000ppm based on the total weight of solids in the dispersion.
- 15 3. Fluoropolymer dispersion according to claim 1 or 2 wherein the anionic surfactant comprises a non-fluorinated anionic surfactant comprising an acid group having a pK<sub>a</sub> of less than 4.
4. Fluoropolymer dispersion according to any of the previous claims, wherein said 20 dispersion comprises said fluoropolymer particles in an amount of at least 30% by weight based on the total weight of the dispersion.
5. Fluoropolymer dispersion according to claim 4 wherein the amount of fluoropolymer 25 particles is between 35% by weight and 70% by weight.
6. Fluoropolymer dispersion according to any of the previous claims wherein the non-ionic emulsifier corresponds to the formula:  
$$R^1-O-[CH_2CH_2O]_n-[R^2O]_m-R^3$$
wherein R<sup>1</sup> represents an aromatic or aliphatic hydrocarbon group having at least 8 30 carbon atoms, R<sup>2</sup> represents an alkylene having 3 carbon atoms, R<sup>3</sup> represents hydrogen or a C<sub>1</sub>-C<sub>3</sub> alkyl group, n has a value of 0 to 40, m has a value of 0 to 40 and the sum of n+m being at least 2.

7. Fluoropolymer dispersion according to any of the previous claims wherein the amount of non-ionic emulsifier is between 1 % and 12% by weight relative to the total weight of solids in the dispersion.
- 5
8. Fluoropolymer dispersion according to any of the previous claims wherein the fluoropolymer particles comprise polytetrafluoroethylene and/or a melt processible fluoropolymer.
- 10 9. Method of providing a fluoropolymer particle dispersion comprising the steps of:
- providing a fluoropolymer dispersion comprising fluoropolymer particles having an average particle size of 10 to 400nm comprising fluorinated surfactant having a molecular weight of less than 1000g/mol or being free thereof;
  - reducing the amount of said fluorinated surfactant in said dispersion if the amount thereof is more than 0.025% by weight based on the total weight of solids of the dispersion;
  - upconcentrating the fluoropolymer dispersion in the presence of a non-ionic surfactant so as to increase the amount of fluoropolymer solids in said dispersion; and
  - adding an anionic surfactant selected from fluorinated anionic surfactants having a molecular weight of at least 1000g/mol, non-fluorinated anionic surfactants and mixtures thereof, to the fluoropolymer dispersion prior to or after upconcentrating said fluoropolymer dispersion.
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- 20
10. Method according to claim 9 wherein said upconcentration is carried out using ultrafiltration or thermal upconcentration.
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11. Method according to any of the proceeding claims wherein the amount of fluorinated surfactant is reduced to below 0.025% by weight by contacting the fluoropolymer dispersion with an anion exchange resin in the presence of a non-ionic surfactant.
- 30
12. Method according to claim 10 wherein the steps of upconcentration and reduction of the level of said fluorinated surfactant proceed simultaneously.

13. Method of coating a substrate comprising the step of coating a fluoropolymer dispersion as claimed in any of claims 1 to 8 on said substrate.
- 5      14. Method according to claim 10 wherein said substrate is selected from a metal substrates, glass fiber fabrics, polymeric substrates and paper.

## INTERNATIONAL SEARCH REPORT

Inte  
nal Application No  
PCT/US 02/25114

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09D127/12 C08F6/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 022 257 A (DU PONT) 14 January 1981 (1981-01-14) cited in the application claims; tables I,III ---	1-8
X	US 4 425 448 A (CONCANNON THOMAS P ET AL) 10 January 1984 (1984-01-10) table I ---	1-8
Y	WO 00 35971 A (SCHWERTFEGER WERNER ;DYNEON GMBH (DE); HINTZER KLAUS (DE); BLAEDEL) 22 June 2000 (2000-06-22) cited in the application claims; examples ---	9-14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the International search	Date of mailing of the International search report
3 December 2002	12/12/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  DE LOS ARCOS, E

## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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